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An NMR study of alkyl exchange reactions between boron and aluminum: effect of such exchange reactions on the polymerizability of alkenyldialkylboranes by the Ziegler–Natta process

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Abstract

Alkyl exchange reactions between boron and aluminum were studied using ^{1}H-NMR, to gain a better understanding of the behavior of various ω-alkenyldialkylboranes towards Ziegler–Natta catalysts. The reaction of a model borane, octyldimethylborane, with Et_3Al, Et_2AlCl and $EtAlCl_2$ was investigated. The transfer of the methyl group from boron to aluminum was monitored as a function of time. The rate of transfer was found to be rapid in the case of Et_3Al and decreased in the order: $Et_3Al \gg Et_2AlCl > EtAlCl_2$. The extent of this transfer at equilibrium, followed the same order and a maximum of 92 mol percent of the methyl group was transferred in the case of Et_3Al. Sterically hindered aluminum alkyls such as tri(isobutyl)aluminum was also found to undergo rapid exchange with octyldimethylborane. Sterically crowded boranes such as 1-hexenyl-9-BBN, however, did not undergo any exchange reaction with Et_2AlCl.

Introduction

Redistribution of alkyl groups in aluminum alkyls has been investigated extensively and is believed to proceed through a mixed bridged dimeric intermediate [1]. Most aluminum alkyls exist as bridged dimers except when the alkyl groups are highly branched and sterically crowded. Trialkylboranes on the other hand exist as monomers and do not undergo exchange reactions at room temperature. Exchange reactions between trialkylboranes and trialkylaluminum compounds, however, was shown to take place readily resulting in the random redistribution of the alkyl groups between aluminum and boron [2]. Such redistributions have also been utilized for the synthesis of some interesting optically active trialkylaluminum

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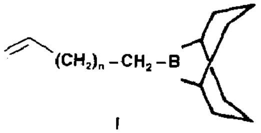
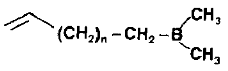
compounds [3]. The equilibrium in such cases is driven to the right by the removal of the more volatile trialkylboranes. When dissimilar groups are present, for example, when trimethylaluminum and tri(1-butyl)borane were allowed to react, a non-random redistribution of the alkyl groups occurred [4].



I



II

We have recently shown that ω-alkenyl-9-BBN (I) can be polymerized by Ziegler-Natta catalysts and can further be converted into poly(alcohol)s [5]. The polymerization catalyst commonly used, is a mixture of $TiCl_3$ and Et_xAlCl_{3-x}. It was observed during our studies, that although the rate of polymerization of 1-octene was slightly retarded in the presence of Et_3B, the molecular weight or molecular weight distribution of the resulting polymer was not significantly altered [6]. Furthermore, the polymerization of alkenylborane monomers I, with $n > 3$, proceeded smoothly to give high yields of the polymer.

Other ω-alkenyldialkylboranes such as ω-alkenyldimethylborane, exhibited a significantly different behavior under similar conditions. For example, 1-octenyldimethylborane II ($n = 5$) does not polymerize under the standard Ziegler–Natta conditions. In order to fully understand this inability of the methylborane monomers to polymerize, we used ^{1}H-NMR spectroscopy to investigate the reaction of a model borane, octyldimethylborane, with a series of aluminum alkyls commonly used as co-catalysts in the Ziegler–Natta process. The implications of such reactions on the ability of alkenylboranes, I and II, to polymerize using Ziegler-Natta catalyst are discussed.

Results and discussion

A series of reactions (eq. 1–3) between 1-octyldimethylborane and Et_xAlCl_{3-x} were carried out in benzene-d_6 at room temperature. The ratio of the alkyl groups on boron and aluminum was kept constant by varying the reactant stoichiometry.

$$\underset{(1/1)}{Et_3Al + RBMe_2} \xrightarrow{\text{very fast}} Et_xMe_{3-x}Al + RBEt_2 \quad (1)$$

$$\underset{(3/2)}{Et_2AlCl + RBMe_2} \xrightarrow{\text{slow}} Et_xMe_{2-x}AlCl + RBEt_2 \quad (2)$$

$$\underset{(3/1)}{EtAlCl_2 + RBMe_2} \xrightarrow{\text{slow}} MeAlCl_2 + EtAlCl_2 + RBEt_2 \quad (3)$$

$(R = C_8H_{17})$

Only the major products are indicated in the above equations. Other minor products formed by self-exchange of the aluminum alkyls and catalyzed self-exchange of the boron compounds are not included in the discussion. In order to establish that

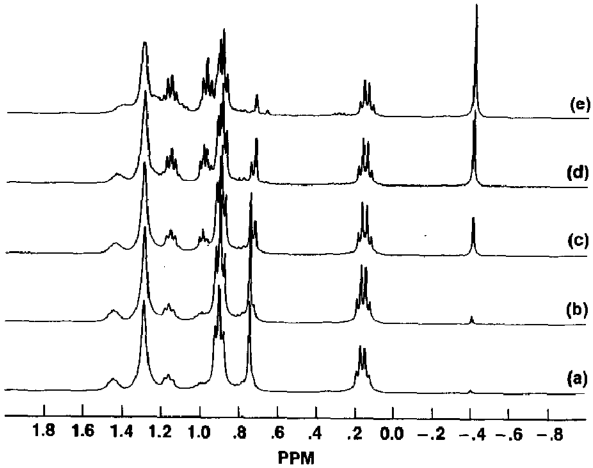


Fig. 1. ^{1}H-NMR spectra of the reaction, $EtAlCl_2 + RBMe_2$, at various times during the reaction. (a) 18, (b) 33, (c) 180, (d) 670, and (e) 2790 min.

exchange of alkyl groups alone occured and no chlorine atom exchange was involved (in the case of eq. 2 and 3), the ^{11}B-NMR spectrum of reaction 2 was recorded. The spectrum showed only a single peak at 85 ppm with reference to $BF_3 \cdot OEt_2$, that corresponds to a trialkyl borane. The absence of a peak at a higher field (78 ppm for neat Et_2BCl [8]) is evidence that the exchange of chlorine does not occur. Furthermore, the transformation of B–Cl compounds to B–C compounds using aluminum alkyls has been shown to be essentially quantitative and has been utilized very effectively as a synthetic tool [9].

The exchange of alkyl groups during the reactions was monitored by ^{1}H-NMR. A typical series of spectra taken at different times during the reaction between $EtAlCl_2$ and $RBMe_2$ is shown in Fig. 1. The transfer of methyl group from boron to aluminum was monitored using the integrated intensities of the peaks at 0.742 ppm (due to CH_3–B) and at −0.408 ppm (due to CH_3–Al). It is observed that as the reaction advances an additional peak begins to appear upfield to the peak at 0.742 ppm. This peak at 0.72 ppm is assigned to the monomethylborane, RB(Et)Me, formed upon the exchange of the first methyl group. The mol percent of both $RBMe_2$ and RB(Et)Me can hence be calculated from the areas of the respective peaks. A plot of these mol percentages versus the mol percent of methyl group transferred to aluminum is shown in Fig. 2. The plot suggests that there is a significant accumulation of the monomethylborane during the initial stages of the reaction, prior to its depletion due to further exchange processes.

The spectra of the reaction mixtures 1, 2 and 3 after equilibrium was attained is shown in Fig. 3. The chemical shifts of the CH_3–Al peak varied because of the formation of different methylaluminum compounds in each of these cases. In the case of Et_3Al the reaction was much faster and equilibrium was attained within 15 min, with 92% of the methyl group transferred to aluminum. The integrated intensities of the peaks due to the methyl groups on boron and aluminum were normalized with respect to the total proton intensity. The total methyl group intensity ($CH_3B + CH_3Al$) remained constant with progress of the reaction. The extent of reaction, represented as the mol fraction of methyl group transferred to

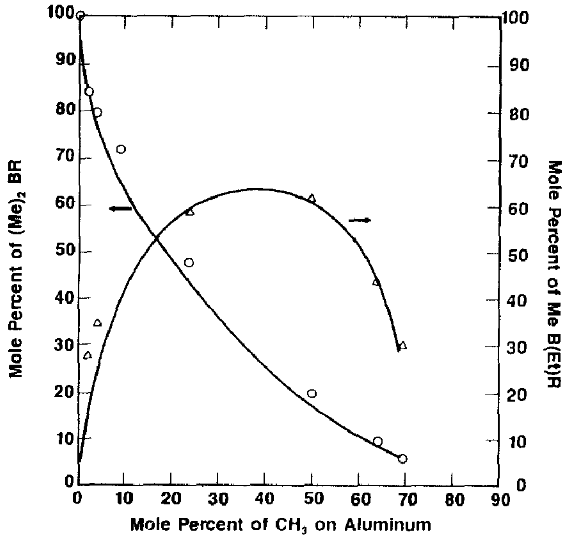


Fig. 2. Plot of the composition of the reaction mixture ($EtAlCl_2 + RBMe_2$) versus mol percent of methyl group transferred to aluminum.

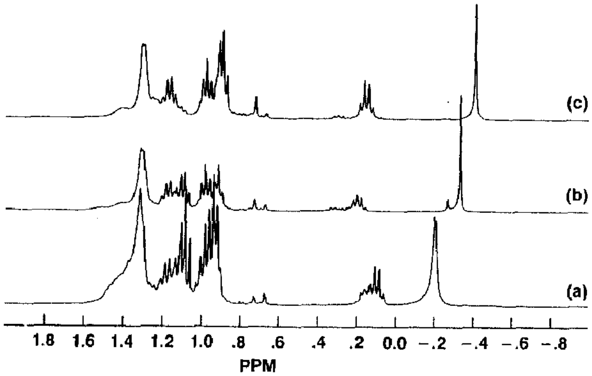


Fig. 3. ^{1}H-NMR spectra of the three reaction mixtures taken after equilibrium was attained. (a) $Et_3Al + RBMe_2$, (b) $Et_2AlCl + RBMe_2$, and (c) $EtAlCl_2 + RBMe_2$.

aluminum, is plotted versus time and is shown in Fig. 4. It is observed that the exchange reaction is very rapid with Et_3Al and decreases in the order; $Et_3Al >$ $Et_2AlCl > EtAlCl_2$. The mol percent of methyl group transferred to aluminum after

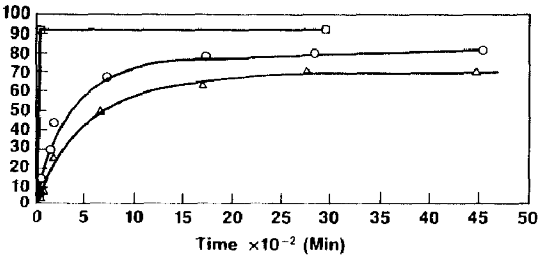


Fig. 4. Plot of mol percent of methyl group transferred to aluminum versus time, for the reactions of $RBMe_2$ with Et_3Al(□), Et_2AlCl(○), and $EtAlCl_2$(△).

equilibrium is attained also followed the same order; with 92% in the case of Et_3Al, 81% in the case of Et_2AlCl and 70% in the case of $EtAlCl_2$.

The exchange of methyl groups between trimethylaluminum and trimethylgallium has been investigated [10,11]. The rate constants for the terminal-bridge exchange of the alkyl groups, and for the intermolecular alkyl exchange between aluminum and gallium were found to be comparable. Based on these and other kinetic data, the rate determining step for the overall exchange process is considered to be the dissociation of the alkylaluminum dimer, Al_2R_6, into the monomer, AlR_3. Unlike the self-exchange between methyl groups in case of mixed alkylboranes such as $RBMe_2$ an additional enthalpy term that governs the equilibrium distribution of the alkyl groups on the boron and aluminum may come into play. The non-random exchange of methyl and ethyl groups in these reactions (1–3) suggests that the methylaluminum compounds formed are more stable than their starting ethylaluminum analogues. There are two plausible explanations for this behavior: one may be a difference in bond energies between CH_3–Al and CH_2–Al, and the second may be due to the greater stability of the dimers formed in the case of the methylaluminum compounds.

We also observe that the transfer of the methyl group from boron to aluminum occurs in a stepwise manner, thereby allowing the accumulation of the monomethylborane, RB(Et)Me (Fig. 2). This is in agreement with the hypothesis that both the bridge-terminal exchange and the intermolecular alkyl exchange occur via a dissociation-association mechanism [10]. Therefore, after the exchange of the first methyl group, both the resulting monomethylborane RB(Et)Me and the starting $RBMe_2$ compete in the further exchange process. If, on the other hand, the terminal-bridge exchange were to occur via a non-dissociative mechanism, one would expect the complete transfer of both the methyl groups to occur (dictated by the enthalpy term), once the bridged intermediate is formed.

The observation, that the rate of exchange is slower in the case of Et_2AlCl and $EtAlCl_2$ as compared to Et_3Al, can also be rationalized on the basis of the above hypothesis. The rate determining step in these cases being the dissociation of the dimers, the slower rate of exchange is probably due to the slower dissociation of the more stable dimers (with chlorine atoms in the bridging positions) formed in the case of the alkylaluminum chlorides.

The final spectrum after attaining equilibrium (Fig. 3), shows a weak triplet between 0.1 and 0.3 ppm (location of the triplet varied with the nature of the aluminum species) slightly down field from the CH_3CH_2–Al quartet. This triplet can be assigned to the methylene hydrogens resulting from the transfer of the octyl group from boron to aluminum. The intensity of this triplet is the largest for Et_3Al and least for $EtAlCl_2$. This is anticipated as Et_3Al was found to be the most reactive of the three.

Aluminum catalyzed redistribution of alkyl groups on boron

In order to understand the ease of transfer of the octyl group from boron to aluminum, octyldimethylborane ($RBMe_2$) was reacted with trimethylaluminum. The ^{1}H-NMR spectrum of the reaction mixture in shown in Fig. 5b. The absence of a triplet between 0.1 and 0.3 ppm confirms the absence of any octylaluminum species in the reaction mixture. The single peak at 0.742 ppm due to CH_3–B, however, splits into three peaks rapidly ($<$ 15 min) upon mixing with Me_3Al and no further change

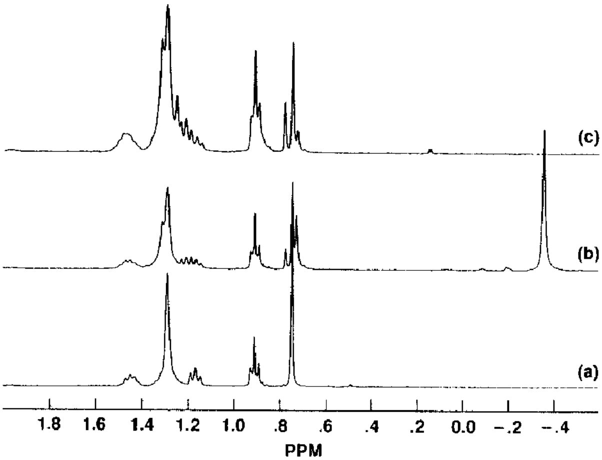


Fig. 5. ^{1}H-NMR spectra of (a) $RBMe_2$, (b) $Me_3Al+RBMe_2$, and (c) $Me_3Al+RBMe_2$ after hydrolysis.

in the spectrum was observed even after 24 h. The total integrated intensity of the three peaks, however, remains unchanged indicating that all the methyl groups are still attached boron. To isolate the irreversible changes that have occurred to the borane, from other kinds of intermolecular interactions with aluminum, the reaction mixture was treated with D_2O. The aluminum alkyls were hydrolyzed and the $Al(OD)_3$ was removed by filtration. The NMR spectrum of the filtrate (Fig. 5c) was found to be identical to that before hydrolysis [12*]. This suggests that a rapid alkylaluminum catalyzed redistribution of the alkyl groups on boron had occurred, leading to the formation of R_3B, R_2BMe, $RBMe_2$ and BMe_3.

The redistribution of the alkyl groups, however, must have occurred by a two step process. First the alkyl group is transferred from boron to aluminum and then back to boron. The absence of any peak corresponding to CH_2–Al in the NMR spectrum (Fig. 5b), however, suggests that the octylaluminum species that is formed is very short lived. The methyl group, therefore, shows a very strong preference for aluminum as compared to an 1-alkyl group such as an octyl group. This is also in agreement with our previous observation in the reactions with Et_xAlCl_{3-x}, that the triplet between 0.1 and 0.3 ppm (due to octyl group on Al) begins to appear only during the later stages of the reaction (Fig. 1). At this time the final product ie., octyldiethylborane (Et_2BR) is present in sufficient quantities and hence the exchange of either of the 1-alkyl groups (ethyl or octyl) with the residual ethylaluminum species become equally feasible.

Sterically crowded alkylaluminums such as tri(isobutyl)aluminum, also undergo very rapid exchange with octyldimethylborane resulting in the transfer of about 84% of the methyl group to aluminum. This suggests that a mixed bridged intermediate is formed in such cases as well. If, however, a bulky trialkylborane such as 1-alkenyl-9-BBN (I) is treated with Et_2AlCl, neither the exchange of alkyl groups, nor the aluminum catalyzed scrambling of the alkyl groups on boron takes place. The steric environment around the boron in this case, presumably does not allow the formation of the bridged intermediate. In addition, the inability of bulky

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* Reference number with asterisk indicates a note in the list of references

aluminum alkyls to form bridges makes the transfer of such bulky alkyls from boron to aluminum also energetically unfavorable.

Behavior of ω-alkenylboranes towards Ziegler–Natta catalysts

It was observed that while 1-octenyl-9-BBN (I, $n = 5$) polymerized readily in the presence of Ziegler–Natta catalyst (typically $TiCl_3/10Et_2AlCl$), 1-octenyldimethylborane does not [13*]. To understand the effect of alkyl exchange reactions on the ability of different ω-alkenylboranes to polymerize, some model polymerizations of 1-octene were carried out in the presence of equimolar amounts of both octyldimethylborane and Et_3B. Both these boranes undergo exchange reactions with the co-catalyst, Et_2AlCl. In the former case the rate of the polymerization was considerably retarded affording only a 51% yield after 24 h, while a yield of above 90% (in less than 2 h) was obtained in the absence of the borane. In the presence of Et_3B, however, the rate was only marginally retarded giving a yield of 83% in 2 h. Under standard polymerization conditions, when the ratio of monomer/Al is greater than 10, a complete transfer of methyl group from boron to aluminum can take place very rapidly in the presence of $RBMe_2$. It has been shown that methylaluminum compounds such as Me_xAlCl_{3-x} are poor co-catalysts for Ziegler–Natta polymerizations, presumably due the sluggish insertion of the first olefin into the CH_3–Ti bond [14]. Thus, the in situ generation of methylaluminum compounds causes the retardation/inhibition of the polymerization of 1-alkenyldimethylboranes. On the other hand, in the presence of Et_3B, although the self exchange of ethyl groups between boron and aluminum does take place, the polymerization rate is not significantly affected. Finally, in the case of the alkenyl-9-BBN monomers (I), no exchange with the alkylaluminum co-catalysts was observed, and hence the polymerizations took place very smoothly.

Conclusions

Reaction of dimethyloctylborane with various aluminum alkyls was investigated using NMR. The methyl groups on boron were transferred to aluminum and the extent of transfer was greatest in the case of Et_3Al, and decreased in the order, $Et_3Al \gg Et_2AlCl > EtAlCl_2$. The rate of the exchange reaction also followed the same order. The dissociation of the aluminum dimers being the rate determining step, the formation of more stable dimers with chlorine atoms in the bridging positions explains this rate order and probably the extents as well. When a mixed trialkylborane such as octyldimethylborane is treated with trimethylaluminum, the transfer of the octyl group to aluminum does not take place. However, aluminum catalyzed redistribution of the alkyl groups on the boron occurs. In the case of sterically crowded trialkylborane, such as alkenyl-9-BBN, neither exchange nor redistribution of the alkyl groups was observed in the presence of Et_2AlCl. The behavior of ω-alkenylboranes towards Ziegler–Natta catalysts has been explained on the basis of these exchange reactions.

Experimental

The aluminum alkyls, Et_3B, Me_3SiCl and lithium dimethylborohydride were purchased from Aldrich Chemical Co. and used directly without further purification. Diethyl ether was distilled over Na-benzophenone ketyl. 1-Octene and 1,7-octadiene were purchased form Aldrich Chemical Co. and distilled over Na-metal prior to use. C_6D_6 was distilled over CaH_2 and degassed, before it was taken into the drybox. The ^{1}H-NMR spectra were recorded in degassed benzene-d_6 using a delay of 30 sec between pulses to allow for complete relaxation. The ^{1}H-NMR spectra were recorded using a 360 MHz Bruker-IBM instrument. ^{11}B-NMR spectrum was recorded using a JEOL FX902 spectrometer and the peaks were referenced to $BF_3 \cdot OEt_2$

Octyldimethylborane. Octyldimethylborane was prepared using the general procedure outlined by Brown and co-workers [7]. The procedure described below was carried out in a dry inert atmosphere (argon) using Schlenk techniques. Lithium dimethylborohydride, $LiBMe_2H_2$ (30 mmol; 60 ml of 0.5 *M* solution in hexanes) was taken in a Schlenk flask and the solvent was stripped off. Thirty milliliters of freshly distilled diethyl ether and 3.3 g (30 mmol) of 1-octene were then added to it. The flask was cooled in an ice-water bath and trimethylchlorosilane (3.8 ml, 30 mmol) was added to it slowly using a syringe. Vigorous evolution of gas (Me_3SiH) was observed. The reaction was allowed to proceed for about 16 h. The volatile components were cryogenically distilled and collected in a flask, leaving behind a white residue of LiCl. The distillate was subjected to fractional vacuum distillation. The required product (1.35 g, 30% yield) was collected as a clear liquid at a temperature of 45–50 °C (at 3–4 mmHg) and was stored under inert atmosphere. The ^{1}H-NMR spectrum of the product was in good agreement with the expected structure. 1-Octenyldimethylborane was synthesized similarly using a 4-fold excess of 1,7-octadiene in the hydroboration step.

Redistribution reactions. The samples for recording the NMR spectra were prepared in the drybox. Typically, 0.12 mmol of octyldimethylborane and 0.5 ml of C_6D_6 were taken in a NMR tube in the drybox under argon and 0.12 mmol of triethylaluminum was added to it using a micro-syringe. The solution was mixed thoroughly at room temperature, and its NMR spectrum was recorded at different intervals. The other reactions were conducted using appropriate mol ratios and maintaining a total molar concentration of the reactants at about 0.5 to 0.6 *M*.

Hydrolysis of the aluminum alkyls. D_2O in a rubber septum capped vial was degassed by bubbling dry argon, using a syringe needle. The alkylaluminum reaction mixture in C_6D_6 was taken in another vial and was capped with a rubber septum. The exit from the D_2O vial was passed through the reaction mixture using a double-tip needle. The slight warming of the D_2O vial caused the saturation of the argon and caused the hydrolysis of the aluminum alkyls. The precipitated hydroxides were removed by filtration through glass wool, and the NMR spectrum of the resulting clear solution was recorded.

Acknowledgement

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